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Microbial electrolytic capture, separation and regeneration of CO₂ for biogas upgrading

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Abstract

Biogas upgrading to natural gas quality is essential for the efficient use of biogas in various applications. Carbon dioxide (CO₂) which constitutes a major part of the biogas is generally removed by physicochemical methods. However, most of the methods are expensive and often present environmental challenges. In this study, an innovative microbial electrolytic system was developed to capture, separate and regenerate CO₂ for biogas upgrading without external supply of chemicals, and potentially to treat wastewater. The new system was operated at varied biogas flow rates and external applied voltages. CO₂ was effectively separated from the raw biogas and the CH₄ content in the outlet reached as high as 97.0±0.2% at the external voltage of 1.2 V and gas flow rate of 19.6 mL/h. Regeneration of CO₂ was also achieved in the regeneration chamber with low pH (1.34±0.04). The relatively low electric energy consumption (≤ 0.15 kWh/m³) along with the H₂ production which can contribute to the energy input makes the overall energy need of the system low, and thereby makes the technology promising. This work provides the first attempt for development of a sustainable biogas upgrading technology and potentially expands the application of microbial electrochemical technologies.

Keywords: Biogas upgrading; Microbial electrolytic system; Bipolar membrane; Biomethane; CO₂ capture and regeneration; Wastewater treatment

Introduction

Biogas as an alternative energy source could contribute to the reduction of fossil fuel utilization and greenhouse gas emissions, and thus, is getting increased attention worldwide (especially in Denmark).¹ Biogas is primarily composed of 60-70% v/v methane (CH_4), 30-40% v/v carbon dioxide (CO_2), and some trace gases such as hydrogen sulfide (H_2S).² Raw biogas with CO_2 presence exhibits a significantly low Wobbe index, heating value and may adversely affect the engine performance.³ Thus, those unwanted impurities especially CO_2 need to be removed from biogas before used as vehicle fuel or injected to natural gas grids. The conventional technologies for CO_2 removal are water scrubbing⁴, pressure swing adsorption, chemical absorption^{5,6}, amine scrubbing, membrane separation⁷, etc. Some of them have several limitations such as high energy requirement, difficulty in recovery of CO_2 , corrosion or clogging problems. Among them, alkaline absorption is characterized of high efficiency, low working pressure, high selectivity and high reaction capacity.⁶ However, the technology still encounters several challenges. In addition to alkali, acids may also be required for further regeneration of CO_2 to reuse/recover the captured CO_2 for subsequent sequestration or synthesis of biofuels and commodity chemicals. Currently, alkali and acids are mainly produced through electrolysis of salt solutions termed chlor-alkali process, which consumes a lot of electrical energy and the transportation to the biogas upgrading plants increases the cost.⁸ Therefore, the high cost of chemicals and safety issues associated with the transportation and storage of chemicals may affect the application of the technology.

In the past years, microbial electrochemical technologies (METs) have gained increasing attention as potentially sustainable approaches for the production of electricity, biofuels or chemicals, and water treatment with low energy investment.^{9, 10} Recently, one of METs, namely microbial electrolysis

desalination and chemical production cell (MEDCC), has been demonstrated as an efficient and cost-effective method for water desalination, acid and alkali production.¹¹ With an external applied voltage up to 1.2 V, pH of 0.68 and 12.9 was achieved in the acid-production chamber and cathode chamber, respectively. Notably, the production cost of alkali in MEDCC was much lower than the market price. Latterly, the feasibility of using the acid and alkali solutions produced by a MEDCC for mineral carbonation and CO₂ sequestration in an external reactor was successfully investigated.¹² However, similar systems, which produce alkali and acids for simultaneous biogas upgrading and CO₂ recovery through absorption and regeneration process, have never been reported. Moreover, a more simplified microbial electrochemical system which could take the advantages of the MEDCC for alkali and acid production should be pursued to reduce the construction costs. Furthermore, the energy intensive aeration associated with the alkali synthesis in cathode (e.g., in MEDCC-like reactor) could be further replaced with energy-gained process such as hydrogen evolution.

In this study, an innovative microbial electrolytic capture, separation and regeneration cell (MESC) was developed as an alternative, efficient and cost-effective approach to realize simultaneous biogas upgrading, CO₂ recovery and wastewater treatment. Such a system consists of an anode chamber, a regeneration chamber and a cathode chamber, separated by a bipolar membrane (BPM) and an anion exchange membrane (AEM), respectively. With an external applied voltage, electrons derived from bacterial oxidation of organic matter transfer from the anode to cathode where H₂ evolution and OH⁻ accumulation occur. Meanwhile, H⁺ and OH⁻ are produced in the BPM through water dissociation, resulting in an acidic environment in the regeneration chamber and neutralization of OH⁻ with H⁺ released from substrate oxidation in the anode chamber. Beside prevention of dramatic pH drop in the anode for better bacterial growth, BPM has the proven potential of more efficient and cost-effective production of acid and alkali in (bio)electrolytic process compared to conventional anion and cation

exchange membranes.^{12, 13} In our system, inlet CO₂ from the biogas is initially captured as HCO₃⁻ and CO₃²⁻ by the alkali solution produced in the cathode (Equation 1 and 2). Because of the potential difference between the middle and cathode chambers, HCO₃⁻ and CO₃²⁻ subsequently transport through AEM to the regeneration chamber where they combine with H⁺ to form CO₂ again (Equation 3 and 4). Therefore, through such process biogas upgrading, CO₂ recovery, wastewater treatment and H₂ production could be achieved simultaneously. The aim of the present study is to demonstrate the feasibility of such novel technology by varying the biogas flow rates as well as the external voltages. The system performance was evaluated in terms of the current output, chemical oxygen demand (COD) removal efficiency, quality of the outlet gas and energy input. This work is among the first attempts to provide proof of concept for a new and value-added microbial electrochemical platform technology for biogas upgrading.



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92 **Material and methods**

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94 **The Setup and Operation of the MESC.** A three-chamber reactor made of nonconductive polycarbonate plates was consisted of the anode chamber, regeneration chamber and cathode chamber which were separated by a BPM (fumasep FBM, FuMA-Tech GmbH, Germany) and an AEM (AMI 7001, Membrane international, NJ), respectively. The working area of both membranes was 25 cm²

(5×5 cm). The working volume of the three chambers was 50, 50 and 100 mL, for the anode, regeneration and cathode chamber, respectively. The reactor was tightened using rubber gaskets and screws to avoid leakage. The anodic electrode is made of carbon brush (5.0 cm in diameter, 5.0 cm in length, Mill-Rose, USA). The cathode electrode is a titanium woven wire mesh (4×5 cm, 0.15 mm aperture, William Gregor Limited, London) coated with 0.5 mg/cm² Pt. A power supply (HQ PS3003, Helmholtz Elektronik A/S, Denmark) was used to provide an additional voltage to the circuit with a 10 Ω external resistance.

The anode electrode was originally pre-acclimated in a two-chamber microbial fuel cell and inoculated with a mixed bacterial culture from domestic wastewater collected from a primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). When stable voltage was obtained around 0.5 V with a 1000 Ω resistance for several cycles, the electrode was transferred into the microbial electrolytic reactor. The anolyte was circulated over a 250 mL recirculation bottle with a peristaltic pump at a flow rate of 25 mL/min. The total anolyte volume was 250 mL. The system was then operated in a batch mode and a continuous mode. The batch experiment lasted for 7 days. During the batch experiment, the recirculation bottle was filled with 250 mL wastewater from the same primary clarifier mentioned before and 5 mL (1 M) sodium acetate was dosed to achieve a COD concentration approximately 2000 mg/L. The regeneration and cathode chambers were filled with 0.05 M sodium chloride solution. Prior to each batch run, all chambers and the recirculation bottle were purged with N₂ for 15 min to ensure anaerobic conditions. The synthetic biogas (60% CH₄ and 40% CO₂) was introduced to the bottom of the cathode chamber by a column diffuser (pore diameters 0.5-1.0 μm, Maltbazzaren ApS, Denmark) via a peristaltic pump at varying gas flow rates. The gas retention time in the chamber was between 3.6-7.5 h according to different gas flow rates. The upgraded biogas was collected from the cathode with a gas bag. The collected gas was recirculated through the cathode

at the same gas flow rate of the raw biogas to enhance the mixing and increase CO₂ absorption. A control experiment without external applied voltage was also operated in the batch mode at 19.6 mL/h gas flow rate. In the continuous mode, the medium in the anodic recirculation bottle was renewed when the current density decreased below 0.8 A/m² while the solution in the regeneration and cathode was not refilled throughout the whole period. The reactor was operated for 40 days with 19.6 mL/h gas flow rate. The external voltage was 1.2 V at the beginning and then increased to 1.4 V and further to 1.5 V at the end. The experiments were carried out at least in triplicate and at room temperature (22±2°C). All chemicals utilized were of reagent grade without purification.

Electrochemical Analyses and Calculations. Voltage drop across the 10 Ω resistance was measured and voltage readings were taken every 30 mins by a digital multimeter (Model 2700, Keithley Instruments, Inc.; Cleveland, OH, USA). Current was calculated according to ohm's law. Current density was calculated as $i=I/A$, where I (A) is the current and A (m²) is the project surface area of the cathode electrode. Conductivity and pH were measured using a CDM 83 conductivity meter (Radiometer) and a PHM 210 pH meter (Radiometer), respectively. Methane and carbon dioxide were determined by a GC-TCD fitted with paralleled column of 1.1 m × 3/16 'Molsieve 137 and 0.7 m × 1/4' with hydrogen as the carrier gas (MGC 82-12, Micolab A/S, Denmark). Hydrogen was analyzed by a GC-TCD fitted with a 4.5 m × 3 mms-m stainless column packed with Molsieve SA (10/80). Cl⁻ was detected via Flame atomic absorptions spectrophotometer (FAAS, Shimadzu). Total inorganic carbon (TIC) was determined by a TC-2000 (Shimadzu, Kyoto, Japan). COD was analyzed according to APHA. Coulombic efficiency (CE), current efficiency (CTE), electric energy consumption by the power source (W_E) and the energy efficiency (η_E) relative to the ratio of produced H₂ energy to the electricity input were calculated as previously described¹⁴ and equations are shown in the supporting

information. Methane loss was calculated as well and the formula is shown in the supporting information.

Results and Discussion

The MESC reactor performance. The microbial electrolytic reactor was first operated with 19.6 mL/h gas flow rate and 1.2 V external voltage. In the control experiment, the reactor was operated in the open circuit at the same gas flow rate. Reactor performance in terms of the current generation, COD removal, pH and conductivity profiles and gas contents was shown in Figure 2.

Figure 2a shows the current output and COD tendency along with the operation time. With 1.2 V external voltage, the current density started at 1.7 A/m^2 and gradually decreased to 1.3 A/m^2 during the first four days since COD in the anode decreased from 2341 ± 320 to $420 \pm 79 \text{ mg/L}$. On day 5, when COD concentration decreased to the level below 500 mg/L , the current density dropped significantly below 0.8 A/m^2 . Therefore, the concentration of organic matter can affect the circuit current by affecting exoelectrogens.¹⁵ Acetate amended domestic wastewater was used in this study as the anodic substrate to proof the concept of the technology. Since METs can use nearly all kinds of organic wastes as substrates, wastewater with high COD levels (e.g., industrial wastewaters and anaerobic fermentation effluents) could be used for practical application of the technology. In the control experiment, a similar COD removal efficiency of $94.4 \pm 1.3\%$ was obtained indicating competitors to exoelectrogens such as methanogen might prevail in the domestic wastewater. Indeed, CH_4 (17%) was detected in the anode chamber for the control reactor. Lower amount of CH_4 (3%) was detected in the closed circuit since exoelectrogens were dominant due to the anode potential¹⁹. Results show the feasibility of the microbial electrolytic system for wastewater treatment. Figure 2b shows the pH

profile of the whole reactor. Initial pH of the wastewater and NaCl solution was 7.30 ± 0.28 and 7.61 ± 0.30 , respectively. In the control experiment, pH in the anode and regeneration chambers changed barely while that in the cathode chamber decreased a little from 7.61 ± 0.30 to 6.32 ± 0.21 . This could be due to CO_2 dissolving in water and the ionization of it to HCO_3^{-16} . When 1.2 V external voltage was supplied to the reactor, pH in the regeneration chamber decreased below 2 which was contributed by water dissociation between the BPM. Anodic pH was nearly stable during the experiment which was due to the neutralization of H^+ from bacterial respiration with OH^- from water dissociation. Catholyte pH first increased to maximum at 9.19 ± 0.12 on the first day and then decreased gradually to 7.42 ± 0.22 on the last day. The increase of the catholyte pH was probably due to the splitting of water for the production of alkaline and H_2 at cathode, which was supported by the observed hydrogen production (37 ± 3 mL) at the end of the batch run. Catholyte pH decreased gradually since dissolved CO_2 reacted with alkaline and generated HCO_3^- and CO_3^{2-} . On day 5 a sharp decrease was observed in catholyte pH which was consistent with the remarkable decrease in the current output. The electrolysis process might cease as organic matter was completely consumed.

The initial conductivity of wastewater and NaCl solution were 2.74 ± 0.23 and 5.72 ± 0.26 mS/cm, respectively. As shown in Figure 2c, in the control experiment conductivity of the reactor fluctuated insignificantly. With 1.2 V external voltage, conductivity in the regeneration chamber first increased from 5.72 ± 0.26 to 22.79 ± 0.75 mS/cm on the second day and then decreased to 11.07 ± 0.95 mS/cm in the end. The increase of conductivity in the regeneration chamber could be explained by H^+ production via the BPM. When pH in the regeneration chamber was 1.34, it could contribute 15.98 mS/cm in conductivity (calculation was stated in Supporting Information). However, along with the decreasing of current density from 1.7 to 0.8 A/m^2 , the water dissociation efficiency decreased even to zero. In Bauer's work²⁰, the water dissociation efficiency decreased from 70% to 0% as the current density drop

from 10 to 0 mA/cm². Another reason for the decrease of conductivity was that carbonate and bicarbonate ions reacted with H⁺ and CO₂ emission occurred. At the end of the experiment, 22±3 mL CO₂ was collected from the regeneration chamber.

Alkaline absorption is an efficient way for biogas upgrading because of the large difference in the solubility of CO₂ and CH₄.¹⁴ As shown in Figure 2d, when no alkaline was produced in the control experiment, the CH₄ concentration was kept around 85% and CO₂ concentration decrease from the original 40% to approximately 15% due to dissolution in water. When 1.2 V voltage was supplied, CO₂ reacted with alkaline leading to a higher CO₂ removal from biogas. For example, the CO₂ concentration was below 8% during the whole period and even to 0.5±0.2% while the highest CH₄ content could be 97.0±1.3%. Therefore, the microbial electrolytic reactor was an efficient approach for biogas upgrading.

Influence of other ionic species on HCO₃⁻/CO₃²⁻ transportation. To achieve efficient CO₂ separation and capture, the key point is to drive HCO₃⁻ and CO₃²⁻ ions through the membrane to the regeneration chamber. However, the cathode was filled with 0.05 M NaCl solution and alkali was produced during H₂ evolution. Cl⁻ and OH⁻ might also move through the membrane and thereby are competing with HCO₃⁻ and CO₃²⁻ for transportation. Therefore, pH and Cl⁻ concentration in the cathode and regeneration chambers were measured along with the operation time. The profile of Cl⁻ concentration is shown in Figure 3. When catholyte pH increased to 9.2, the OH⁻ concentration was as low as 1.58×10⁻⁵ M and therefore would have insignificant effect on electron flux balance. As shown in Figure 3 and Table S2, no significant changes in Cl⁻ concentrations were observed in the regeneration chamber and cathode chamber in the open circuit. On the first day of the closed circuit operation, when current densities were the highest and HCO₃⁻ concentration was the minimum, the Cl⁻ concentration reached the maximum of 2404±50 mg/L followed by a slightly decrease in the regeneration chamber. In the cathode, the Cl⁻ concentration decreased to 1040±40 mg/L to compensate the flux of electron

which was consistent with the slightly lower conductivity (4.69 ± 0.17 mS/cm) on the first day. Subsequently, the slight transfer of Cl^- from the regeneration chamber to cathode chamber occurred due to back diffusion or ion exchange with $\text{HCO}_3^-/\text{CO}_3^{2-}$. The final Cl^- concentrations in the regeneration and cathode chamber in the closed circuit were 0.053 and 0.045 M, respectively. Results indicated the final flux of Cl^- transported from the cathode to the regeneration chamber was limited ($\leq 10\%$). It has been reported that ion transfer can be prevented due to similar ion concentrations in both compartments separated by the membrane^{17, 18}. According to the C balance shown in Figure 5, at the end of the batch test 0.261 g of TIC was detected in the regeneration chamber in closed circuit which equals equivalent of 0.022 mol HCO_3^- . A current efficiency of 81% could be achieved during the whole period meaning that the transfer of every mol of electrons to the cathode was accompanied by 0.81 mol HCO_3^- transportation. Thus, the HCO_3^- transportation would not be adversely affected by Cl^- and OH^- .

Effects of the gas flow rate and applied voltage on the system performance. The influence of biogas flow rate on the system performance was investigated at the external voltage of 1.2 V. The gas flow rate was control by the peristaltic pump from 13.4 to 27.7 mL/h. The summary of current outputs, pH and conductivity profiles, and outlet gas composition during the experiment is shown in Figure 4.

Under different gas flow rates, the current density showed similar trend along with the operation time (Fig. 4a). The current density fluctuated around 1.6 A/m^2 and significantly dropped below 0.8 A/m^2 after the fourth day due to the substrate consumption and high polarization resistance of the BPM. The current output was mainly influenced by the microorganism community and the substrate concentration. However, with 13.4 mL/h gas flow rate, the reactor produced relatively lower current densities. Since gas introduction to the catholyte might function as mixing and enhance the mass transfer. Relatively low gas flow rate and recirculation rate resulted in small disturbances and slow mass transfer which was adverse to the cathodic hydrogen evolution.

In Fig 4b, cathodic pH was in the range of 7 to 10 while pH in the regeneration chamber was between 1.5 and 4. With the gas flow rate increasing, cathodic pH decreased obviously indicating the enhanced CO₂ absorption in the alkaline solution. With 13.4 mL/h gas flow rate, it was found that cathodic pH reached the highest value around 10 on the second day. It is because relatively less CO₂ reacted and consumed OH⁻. In Fig. 4c, the maximum conductivity in the regeneration chamber increased from 14.08±0.75 to 22.79±0.75 mS/cm along with the increasing of gas flow rate from 13.4 to 19.6 mL/h. When the gas flow rate went up further, conductivity did not increase further. Correspondingly, when the gas flow rate was below 20 mL/h, CH₄ composition kept above 90% and could reach to maximum at 98.1±0.2%. CO₂ was removed effectively and could be lower than 2% during the first 4 days when the gas flow rate was below 20 mL/h. When the gas flow rate increased from 25.3 to 27.7 mL/h, CH₄ composition dropped from 88% to 84% as average during the whole period. Therefore, a proper feeding gas flow rate is crucial to improve the system performance. When the gas flow rate was low, the biogas upgrading capacity might decrease while high flow rates might decrease the purity of CH₄. Further strategies for the improvement of biogas flow rate are thus required in future studies for accelerating the commercialization.

The effect of external voltage on the CO₂ removal efficiency and CH₄ enrichment was studied. The system performance was compared at external voltage of 0, 1.0, 1.2 and 1.4 V which are shown in Figure S1 and S2. When the gas flow rate was the same but the external voltage elevated, the maximum catholyte pH was increased from 6.44±0.05 (0 V, 19.6 mL/h), 7.37±0.12 (1.0 V, 19.2 mL/h) to 9.19±0.11 (1.2 V, 19.6 mL/h) and from 7.38±0.08 (1.2 V, 27.7 mL/h) to 7.52±0.10 (1.4 V, 28.0 mL/h) as well as the volume of generated H₂ from 0 mL (0 V, 19.6 mL/h), 22±2 mL (1.0 V, 19.2 mL/h) to 37±3 mL (1.2, 19.6 mL/h V) and from 37±3 mL (1.2 V, 27.7 mL/h) to 40±3 mL (1.4 V, 28.0 mL/h), respectively. The applied voltage would induce fast electron transfer kinetic and compensate the

electrode overpotential, which could also enhance the substrate consumption by anode respiring bacteria²¹ and favorite the electrolysis process. When the applied voltage was changed from 0, 1.0 to 1.2 V at around 19.6 mL/h gas flow rate, the maximum CH₄ content of the output gas increased from 85.5±0.3%, 89.2±0.4% to 97.0±0.2%. However, when the gas flow rate was higher than 25.3 mL/h, the concentration of CH₄ could not be improved further with even higher applied voltage (1.4 V). The biogas upgrading capacity probably has a threshold and the system performance might be determined by other limiting factors.

Experimental results at various operation conditions are summarized in Table 1. As shown in Figure 4a, with the fixed external voltage supply (1.2 V), the current density increased along with the increasing of gas inflow rate since it enhanced the mixing and mass transfer. However, cathodic pH and upgrading performance showed opposite trends (Figure 4b and 4d). It could be due to a change in equilibria between alkali production capacity at cathode (expressed as pH) and the dissolving gasses. In this case, the gases dissolution rate was higher than the OH⁻ generation rate. As expected, the current density, cathodic pH and upgrading performance increased with the increasing external voltage supply (Figure S1 and S2). However, the increase in those parameters turned to be limited when the gas inflow rate was over a certain level. Thus, operational parameters applied such as voltage and gas inflow rate need to be better adjusted to maintain equilibrium between cathodic pH and the dissolving gasses for efficient upgrading. Considering the final pH and Cl⁻ concentration in the cathode (Table S2), the changes in the transportation of other anions than HCO₃⁻ and CO₃²⁻ were not significant under the tested conditions. The collected CO₂ increased with the current density since more HCO₃⁻ ions were transported via the membrane driven by higher current and then CO₂ was formed at the lower pH. Results indicate that both the applied voltage and biogas flow rate are crucial to the system

performance. Eligible CH₄ content (>90%) was obtained when the gas flow rate was in the range of 13.4 and 19.6 mL/h with 1.2 V applied voltage.

Energy analysis and mass balance. The electrical energy consumption for biogas upgrading technologies is an important issue for the practical application. Our lab-scale system consumed between 0.09 and 0.15 kWh of electrical energy for upgrading one m³ raw biogas, which was quite competitive compared with commercial technologies. For instance, the electricity demand for biogas upgrading is about 0.2-0.32 kWh/Nm³ raw gas with water scrubbing, 0.1-0.15 kWh/Nm³ with chemical absorption and 0.15-0.22 kWh/Nm³ with membrane technology^{3, 22}. It should be noted that the electricity consumption is the sole “consumable cost” of microbial electrolytic system for biogas upgrading while additional of chemicals (e.g., acids and alkali), high pressure or temperature are required in most of the conventional methods. Since the microbial facilitated release of electrons stored in organic matter from wastewater, the applied voltage was much lower than that used in the water electrolysis process.¹⁴ Moreover, an energy carrier (H₂) is produced in the cathode which could substitute 21-27% of the electric energy input. Since the substrate was degraded and about 16-33% of the chemical energy was converted to the electrical energy, the energy provided by the organic substrate was 140-334 kJ/Nm³ which was calculated according to the energy content of acetate based on the heat combustion. The energy benefits could be even higher if energy savings for wastewater treatment was considered. Besides operational and maintenance costs for in real scale application, investment should also be considered. However, investment costs per m³ raw biogas would decrease with increasing capacity.

At the end of the batch run with and without 1.2 V external voltage at 19.6 mL/h gas flow rate, carbon balance was performed to study the carbon capture mechanism. Rude biogas was introduced into the reactor as the source of CO₂. In the cathode, CO₂ was converted to (bi)carbonate and

transported to the regeneration chamber. Then (bi)carbonate reacted with H^+ and CO_2 was regenerated. Volume of initial CO_2 and regenerated CO_2 was measured and TIC of the solution was determined. The carbon balance is shown in Fig. 5. In the control experiment, approximately 30% of the CO_2 was remained and 16% of the CO_2 existed in the cathode chamber as the form of soluble $NaHCO_3$ and Na_2CO_3 . No CO_2 was collected from the regeneration chamber since acid was not produced. When an external voltage of 1.2 V was supplied, carbon distribution was quite different. The remained CO_2 in the outlet accounted for 15% of the total initial CO_2 and 37% existed as (bi)carbonate in the regeneration chamber. The regenerated CO_2 and TIC in the cathode chamber shared 2% and 12% of the initial carbon, respectively. The imbalance on CO_2 species could be due to diffusion to the anode and measurement error.

Experiment under the continuous mode. The microbial electrolytic system was then operated in the continuous mode for 40 days. For the initial 26 days the system was operated with 1.2 V external voltage and 19.6 mL/h raw biogas flow rate. The external voltage was increased to 1.4 V since day 26th and enlarged further to 1.5 V from day 33rd to the end of the experiment at the same gas flow rate. CH_4 , H_2 and CO_2 contents in the outlet gas in the continuous mode are showed in Figure 6. During the first six days, CH_4 content was above 90% and could reach $97.5 \pm 0.74\%$ at maximum while CO_2 content was below 5% and reached $1.0 \pm 0.48\%$ at minimum. Subsequently, CH_4 and CO_2 content were kept around 88.3% and 8.3%, respectively. During the whole period, H_2 was produced and the content was around 3.8%. Approximately, 18.8 L rude biogas was treated and the energy consumption for per m^3 raw biogas was 0.18 ± 0.01 kWh. During the 40 days operation, NaCl solution has not been changed and the saturation state was not reached yet, which shows a huge absorption capacity of our system with less maintenance. When the external voltage was increased to 1.4 V and 1.5 V, a peak occurred at the corresponding CH_4 content. However, the enhancement on the biogas upgrading was limited which

indicated that there were probably other limiting factors dominating the system performance other than external voltage in the continuous mode. Membranes were not cleaned or replaced during the whole period which exhibits the tolerance of membranes.

This study for the first time demonstrated the proof of concept of a microbial electrolytic system for simultaneous CO₂ capture, separation and regeneration, biogas upgrading and wastewater treatment. Compared to commercial biogas upgrading technologies, the novel system developed here has several merits. First, addition of chemicals is not needed since acid and alkaline are generated and utilized in situ which saves the cost/risks for chemicals transportation and storage. Secondly, methane loss (e.g., due to dissolution) during the whole period is less than 1.4% while that in traditional biogas upgrading technologies is about 2%^{3,23}. Low methane loss is beneficial for economic and environmental aspects. Thirdly, separated CO₂ from rude biogas and the (bi)carbonate solution can be further used in other industrial applications, such as the production of algal biomass and enhanced oil recovery.³ Moreover, the applied voltage to overcome the thermodynamic barrier of water splitting in our system is quite lower than that used in the abiotic water electrolysis. It is because the chemical energy stored in the organic matter was released with the help of bacteria to offset the difference. Organic substrates provided energy to the system instead of consuming energy. However, it was not counted as energy input since the wastewater has to be treated anyway. Therefore, the electrical energy consumption in the system is quite low (0.09 kWh/Nm³) and H₂ produced can even substitute part of the energy costs (up to 27%). In addition, the MESC as biological system could meet the needs of sustainability and circular economy. The simple configuration of the MESC makes the technology more competitive compared to the traditional electrolysis processes and MEDCC for the purpose of biogas upgrading and CO₂ recovery. However, for practical applications, several issues should be considered. For instance, H₂S and other impurities in biogas should be removed (biogas pre-upgrade) in advance to eliminate the

risk for adverse effect on the microbial electrolytic system. Acetate amended real domestic wastewater was used here to prove the concept. Many waste streams such as industrial wastewater or fermentation effluent have high COD concentrations and can potentially be used for practical application of the technology. Despite long term operation of the microbial electrochemical system with domestic wastewater (amended with acetate), for more than half year, biofouling of the membranes was not observed. Furthermore, NaCl as electrolyte in this study may add the operational costs. However, in practical application, NaCl can be added once to start up the process rather than continuous addition. Wastewater, which could support the conductivity in the liquid during continuous operation, may substitute NaCl. Taking this into account, the energy costs could be further reduced, and thus, further improvement such as appropriate material selection and chemicals refusal might be necessary. To conclude, the concept is very challenging but also full of promises and is definitely going to make a significant impact on relative research field.

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Supporting Information

Calculation for Coulombic efficiency (CE), energy efficiency, current efficiency and methane loss. Table S1, Table S2, Figure S1, and Figure S2 as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org/>

Author Contributions

[#]X.J. and Y.Z. contributed equally to the paper.

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427 **Table 1.** Experimental results at various operation conditions

Voltage V	0	1.0	1.2			1.4	
Gas flow rate mL/h	19.6	19.2	13.4	19.6	25.3	27.7	28.0
pH _{max} in Cathode	6.44±0.05	7.37±0.12	10.03±0.07	9.19±0.11	8.59±0.10	7.38±0.08	7.52±0.10
pH _{min} in Regeneration	6.87±0.04	2.09±0.07	1.88±0.05	1.34±0.04	1.43±0.10	1.36±0.07	1.44±0.06
Max CH ₄ %	85.5±0.3	85.9±0.4	98.1±0.2	97.0±0.2	90.3±0.3	86.0±0.3	86.1±0.2
CO ₂ removal efficiency %	78.3±1.4	77.0±0.7	98.7±0.5	92.6±0.6	89.3±1.5	85.7±.04	81.3±1.1
COD removal efficiency %	94.4±1.3	80.4±2.7	78.7±3.5	98.2±2.6	91.9±2.8	93.4±4.7	86.5±5.9
CE %	-	16.3±1.4	20.0±1.3	26.0±2.1	22.7±1.7	32.6±1.3	17.5±1.8
CO ₂ collected mL	-	6±3	10±3	22±3	18±2	24±2	25±2
H ₂ mL	-	22±2	24±2	37±3	32±2	31±4	40±3
Electricity consumption kWh/m ³		0.09±0.004	0.15±0.003	0.15±0.003	0.10±0.003	0.11±0.002	0.13±0.004
Energy efficiency	-	26.8±1.2	24.2±1.7	26.5±0.8	26.7±1.4	20.6±1.7	22.4±2.2
CH ₄ loss %	1.22±0.02	1.32±0.03	1.21±0.02	1.23±0.02	1.14±0.03	1.20±0.02	1.27±0.02

428 **Figure Caption**

429 **Figure 1.** The schematic diagram of MESC. BPM, bipolar membrane; AEM, anion exchange membrane.

430 **Figure 2.** MESC performance at 19.6 mL/h gas flow rate with 1.2 V and control experiment. A, anode chamber;
431 R, regeneration chamber; C, cathode chamber. The current density output and COD changes (a); pH
432 profiles in three chambers (b); conductivity profiles in three chambers (c); methane and carbon dioxide
433 contents in the outlet gas (d).

434 **Figure 3.** Profiles of Cl^- concentration in the regeneration chamber and cathode chamber along with the
435 operation time.

436 **Figure 4.** MESC performance with 1.2 V and varying gas flow rates. The current density output (a); pH profiles
437 in the cathode (C) chamber and the regeneration (R) chamber (b); conductivity profiles in the
438 regeneration chamber (c); methane and carbon dioxide contents in the outlet gas (d).

439 **Figure 5.** Carbon balance in MESC system with and without 1.2 V external voltage at 19.6 mL/h gas flow rate.

440 **Figure 6.** Methane, hydrogen and carbon dioxide contents in the outlet gas in the continuous mode.

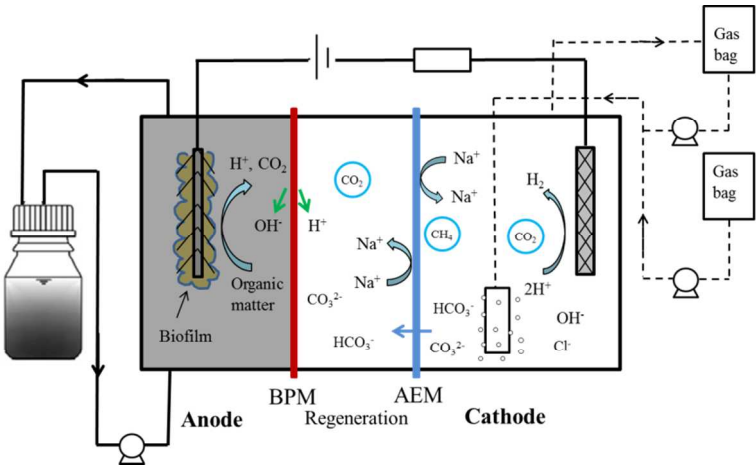


Figure 1

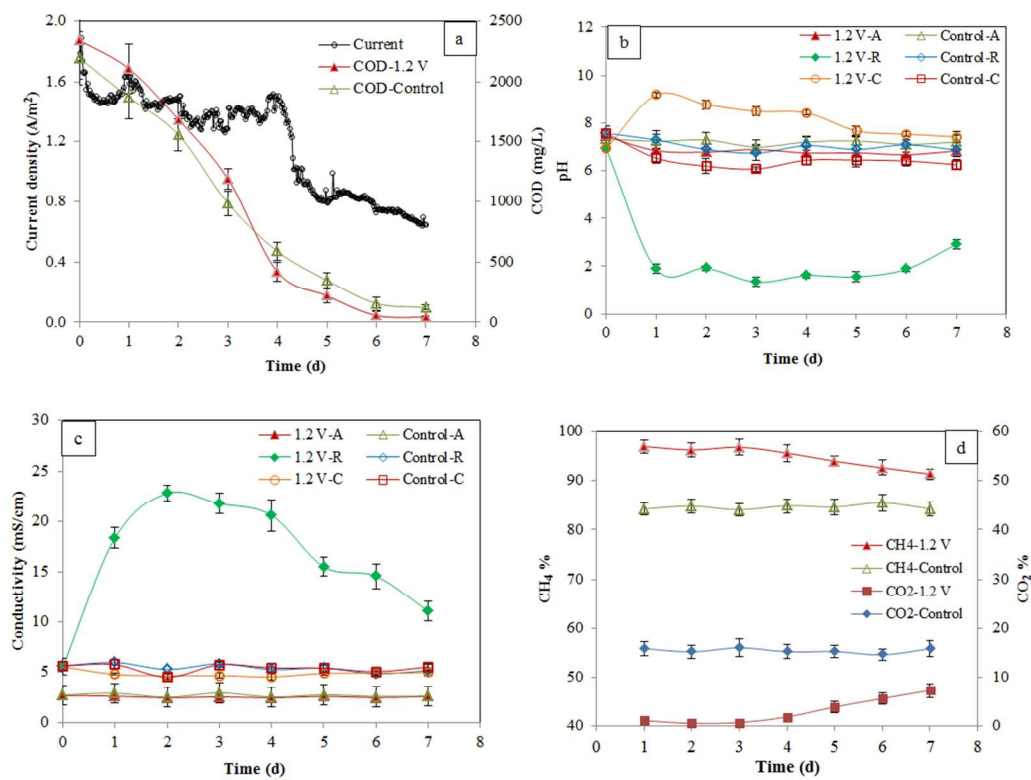


Figure 2

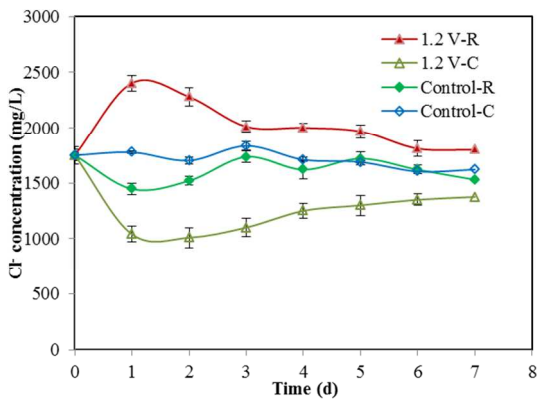


Figure 3

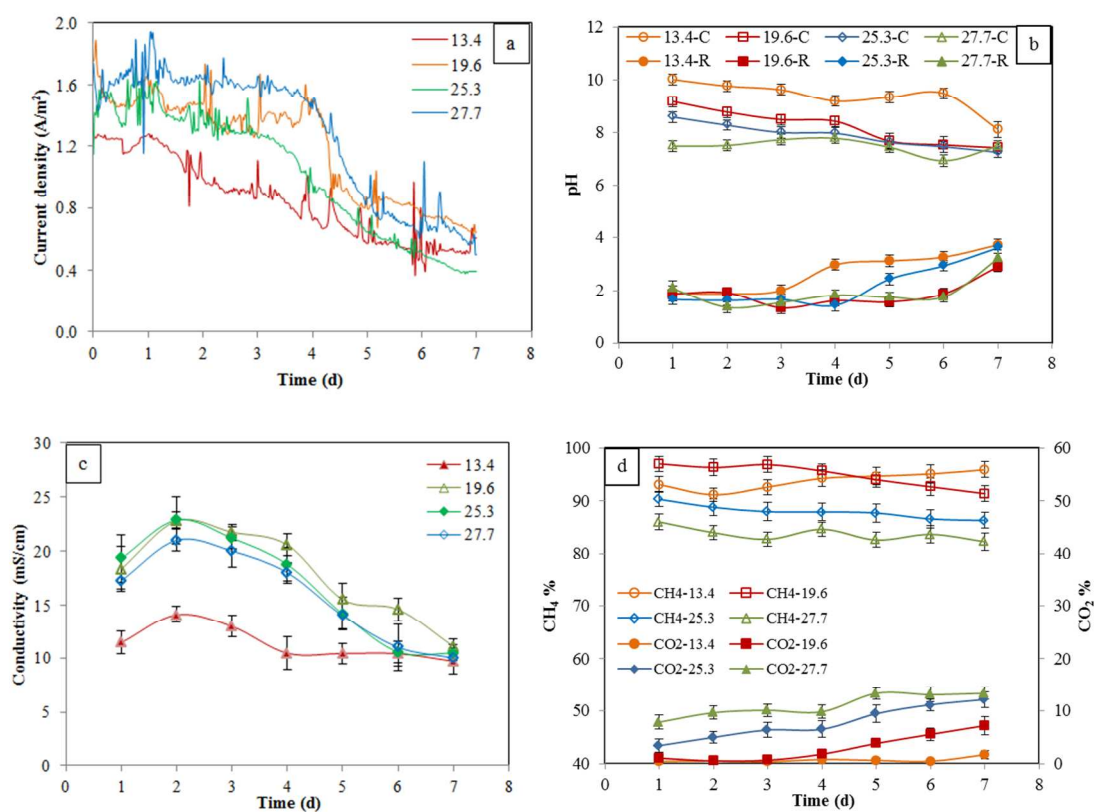


Figure 4

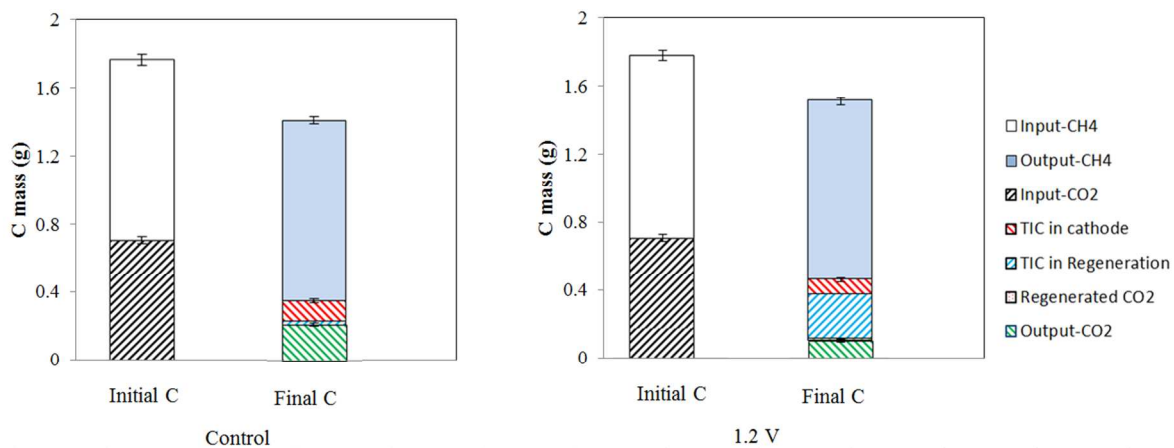
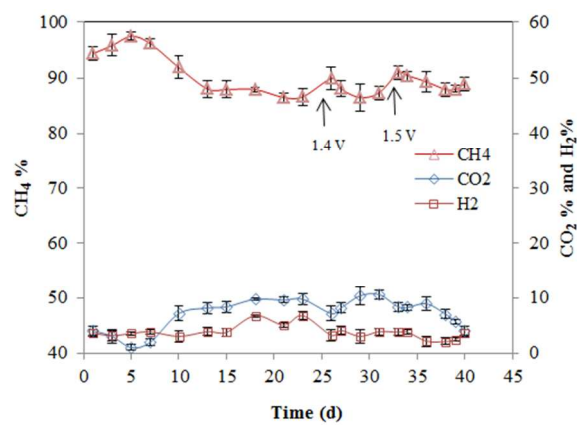


Figure 5

**Figure 6**

455 TOC art

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